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Removal of pesticides from white and red wines by microfiltration

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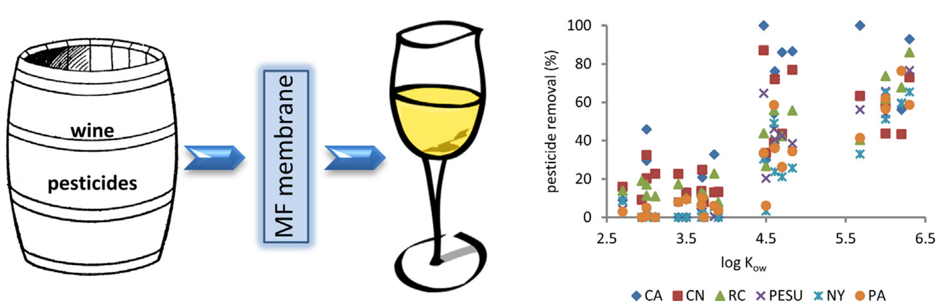
HIGHLIGHTS

- Various mixtures of 23 pesticides were determined by SPE and GC-ECD in wine.
- The removal of pesticides is affected by the type of membrane and wine.
- The higher the pesticide's hydrophobicity, the higher its removal.
- Antagonistic and synergistic effects of pesticides in wines were estimated.

GRAPHICAL ABSTRACT



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ABSTRACT

The aim of this work is the investigation of microfiltration in removing pesticides from a white and a red Greek wine. Six membranes with pore size 0.45 μm were investigated. Two mixtures of 23 and 9 pesticides, and single pesticide solutions were added in the wine. The pesticides tested belong to 11 chemical groups. Solid phase extraction (SPE) followed by gas chromatography (GC) with electron capture detector (ECD) were performed to analyze pesticide residues of the filtered fortified wine. Distinct behavior was exhibited by each membrane. Cellulose acetate and cellulose nitrate showed higher mean pesticide removal for both wines, followed by polyethersulfone, regenerated cellulose, and polyamides. The filtration effectiveness was correlated to the membrane type and to the pesticide chemical structure and properties (octanol-water partition coefficient, water solubility) and compared for the wines tested. In most cases, the more hydrophobic pesticides (pyrethroids and aldrin) showed higher removal from red wine than white wine. Adsorption on membranes was increased by increasing hydrophobicity and decreasing hydrophilicity of organic pesticide molecule. The removal of each pesticide from its single solution was generally higher than that from its mixtures, allowing the estimation of the antagonistic and synergistic effects of pesticides in the mixtures.

1. Introduction

Serious problems have arisen by the use of pesticides for both the environment and human health. However, the crop protection with chemical methods is an essential practice in viticulture for wine making, due to the specificities of the cultivation of the vine and its diseases and pests. Pesticide number, type and quantities applied on grapes vary significantly every year, depending on climate conditions, enemies' growth, wrong application from the

Abbreviations: AEI, antagonistic (or synergistic) effect index; CA, cellulose acetate; C_m, capacity of each membrane; CN, cellulose nitrate; K_{ow}, octanol-water partition coefficient; MPR, mean pesticide removal; MRL, maximum residue limit; MRSP, mean removal of significantly removed pesticides; N, total number of pesticides; NY, nylon; PA, polyamide; PESU, polyethersulfone; PR, pesticide removal; RC, regenerated cellulose; S_m, selectivity of each membrane; TAEI, total antagonistic effect index; TSEI, total synergistic effect index.

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producer etc. Many pesticide residues are often detected in grapes and wine, depending on the quantity of their use in the field, the way, the number of applications and the time from application to harvest.

Many researchers have found that winemaking processes (maceration, pressing, racking, clarification and filtration) reduce the concentration of pesticide residues to some extent [1–10]. The effect of pesticide properties, particularly water solubility [11–20] and octanol-water partition coefficient (K_{ow}) [16,18–20], on the persistence of pesticides from the vine to the wine, during winemaking, has been examined in a limited extent. Particularly, so far, microfiltration has not been investigated in winemaking process or separately, systematically and in depth. Few research works are reported on microfiltration for pesticide removal from wines, including a limited number of membranes (mostly nylon) and pesticides examined [12,15,16,20]. The reduction or the elimination of pesticide residues from wines using filtration, as the last step of winemaking, was proved effective [12,15,16,20]. The correct choice of filtration (following clarification) is an effective way of removing pesticide residues, useful for winemakers, since they assure the hygienic and sanitary quality of wines. In addition, the data provided are useful for the estimation and prediction of efficiency of filtration in reducing pesticide residues, and the preparation of legislation norms on maximum residues limits (MRL) in wines, which might include correction factors for the winemaking processes employed [15]. The study of pesticide removal from wines by membrane filtration could be useful for similar water-systems contaminated with pesticides, beyond wines. MRLs have not been established in wine by the EU, but only in wine grapes [21]. In addition, the pesticide minimum requirement for drinking water is set at 0.1 μg/L for each pesticide and 0.5 μg/L for total pesticides [22].

A great number of multiresidue methods for determining pesticides in agricultural products and especially wine is reported in the relevant literature. Most of these methods used are gas chromatography (GC) with nitrogen–phosphorus (NPD), electron-capture (ECD) or mass spectrometry (MS) detectors and liquid chromatography (LC) with ultraviolet (UV), diode-array (DAD) or MS detectors. These methods are mainly based on liquid-liquid extraction (LLE), solid-phase extraction (SPE), or microextraction (SPME), stir bar sorptive extraction (SBSE), single-drop microextraction (SDME) [23–26].

The aim of this study was to determine the potential of microfiltration membranes (cellulose acetate, cellulose nitrate, regenerated cellulose, polyethersulfone, nylon, and polyamide) to remove the pesticides from a white and a red wine. Two mixtures of 23 and 9 pesticides, and single pesticide solutions were added into the Greek white and red wine, varieties Savvatiano and Agiorgitiko respectively. The 23 pesticides examined were aldrin, bifenthrin, bromophos, chlorpyriphos, cyfluthrin, deltamethrin, dichlobenil, dichlofluanid, fenarimol, fenhexamid, flucythrinate, folpet, hexaconazole, kresoxim-ethyl, lindane, myclobutanil, oxyfluorfen, penconazole, procymidone, tetradifon, trifloxystrobin, trifluralin, vinclozolin. These pesticides are representable of various chemical groups with different properties. The effect of the membrane type, and the pesticide's chemical structure and properties (K_{ow}, water solubility) on the microfiltration performance was investigated. The antagonistic and synergistic effects, occurring among the pesticides in the mixtures, were estimated.

2. Experimental

2.1. Wines

Two non-clarified and non-filtered wines, produced from the white Greek varieties Savvatiano and Agiorgitiko were used. The white wine has the following characteristics: pH = 3.26, alcohol 11.75% v/v, volatile acidity 0.22 g/L, total acidity 5.2 g/L, reducing sugars 1.1 g/L, SO_2 free 29 mg/L, SO_2 total 95 mg/L. The red wine has the following characteristics: pH = 3.48, alcohol 12,96% v/v, volatile acidity 0.54 g/L, total acidity 5.97 g/L, reducing sugars 0,75 g/L, SO_2 free 28 mg/L, SO_2 total 80 mg/L.

2.2. Microfiltration membranes

Six microfiltration membranes with the same pore size 0.45 μm were used. Cellulose acetate (CA), cellulose nitrate (CN), regenerated cellulose (RC), polyethersulfone (PESU), and polyamide (PA) were purchased from Sartorius, while nylon (NY) was purchased from GE Magna. All the membranes examined have a hydrophobic hydrocarbon network chemically connected with a number of specific hydrophilic groups characterizing each membrane (i.e. −OH, −CO, $-NH_2$, −OSO).

2.3. Pesticides

Certified reference standards of the 23 pesticides tested were of >96% purity. All pesticides were purchased from Dr Ehrenstorfer GmbH, with the exception of vinclozolin purchased from Sigma, and flucythrinate purchased from Chem service with 93.1% purity. The selection of 23 pesticides tested was based on a number of criteria: the probable use of these pesticides in viticulture, the representation of 11 chemical groups of pesticides including fungicides, insecticides, herbicides (e.g. organophosphorus, organochlorines, pyrethroids, azoles etc.), and the great range of their properties (MW from 172 to 505, log K_{ow} from 2.7 to 6.3, and solubility from 0.0002 to 142 mg/L). MRLs in wine grapes for 23 pesticides examined range from 0.01 to 15 mg/L. It should be noticed that the investigation of a filtration of a pesticide acidic aqueous solution, containing a number of pesticides, could be valid for similar systems beyond wines, considered as a "black box".

2.4. Reagents

Acetone and ethyl acetate were of analytical grade for pesticide residue analysis. Ethanol absolute for analysis and water for chromatography were also used.

2.5. Solution preparation

Stock solutions, 1000 mg/L, of individual pesticide standards were prepared in the appropriate solvent, acetone or methanol. The stock solutions were stored at low temperature (−20 °C) in vials with Teflon lids that prevent any loss of solvent. Intermediate stock solutions, 100 mg/L, and intermediate stock mixtures, 20–100 mg/L were also stored at low temperature (−20 °C) for maximum 12 and 2 months respectively. Two mixtures of pesticides were prepared, the first containing 23 pesticides and the second 9 selected pesticides representing 9 main chemical groups. In addition, single solutions of pesticides were made. Wine was collected from a barrel into 5 L glass bottles and then was divided into smaller sample volumes (75 mL), after agitation. Each wine sample was fortified, through intense stirring, with appropriate volume of the intermediate stock pesticide mixtures and single solutions, to achieve the concentration of 0.1 mg/L for each pesticide.

The initial total pesticide concentration was 2.3 mg/L in the mixture of 23 pesticides, 0.9 mg/L in the mixture of 9 pesticides in wine and 0.1 mg/L initial concentration for each pesticide either in mixtures or single solutions. Similar pesticide total or single concentrations levels in winemaking processes (i.e. clarification) have been examined [14,18]. The concentration of 0.1 mg/L for each pes-